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ANALYTICAL TECHNIQUES FOR CHARACTERIZATION OF OIL SHALES

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INTRODUCTION

Oil shale, a fine grained sedimentary rock containing insoluble organic material that yields oil by destructive distillation, or retorting, occurs in large quantities in many parts of the world and in the United States. The identified resources of shales outside the United States total over 1.1 trillion barrels of oil (1). The richest deposits in the United States are located in the Eocene Green River formation of Colorado, Utah and Wyoming. In part of this formation, the Piceance Basin, the oil shales are thought to contain energy equivalent of about 1.2 trillion bbl of oil, or about 40 times the nation's present proven reserves of petroleum. Environmental issues associated with shale retorting require substantial monitoring and control of waste products, which can be quite large.

At Exxon Research and Engineering Company's Baytown Research and Development Division, analytical methods for coal and coal products have been developed and are being used (2-4). These methods are now being extended to the characterization of oil shales. This extension is not straightforward in all cases because in several respects shale is almost the exact opposite of coal. For example, shale is high in inorganics and low in organics, the opposite of most coals and shale organics have a high H/C ratio, also the opposite of coal.

The major analytical techniques used for shale analysis are neutron activation analysis (5), X-ray fluorescence (5), and atomic spectroscopy (6-8). In the present paper, we are describing our approach to the multi-element analysis of oil shales and their products utilizing mainly inductively coupled plasma emission spectrometry (ICPES) for metals, and ion chromatography (IC) for some nonmetals. Other major elements such as carbon, hydrogen, nitrogen, sulfur and oxygen, are determined by a variety of combustion techniques.

EXPERIMENTAL

Shale Preparation

The oil shale samples were pulverized to -100 mesh before sampling. Aliquots of the samples were ashed at 750°C for 5 hrs in a muffle furnace. Kerogen was isolated from the shale samples by demineralization with HCl and HF, a procedure developed at the U. S. Bureau of Mines (19).

Parr Bombs

Two types of Parr bombs were used. The acid digestion bombs were used for the ash dissolutions. About 0.2 g of shale or ash was dissolved in 3 mL aqua regia and 2 mL HF in the Parr bomb and heated at 110°C in an air-oven for 2 hours. After the dissolution, 1 g of boric acid was added to each sample solution which was heated on a water-bath for 15 minutes. If any unburned carbon was visible, the solutions were filtered; otherwise, they were diluted to 100 mL. A blank containing the same amounts of the acids was also prepared. The Parr oxygen bombs were used for a rapid ash determination and for sample preparation for IC. About 0.5 g of shale or shale oil was mixed with 0.5 g of white oil in a stainless steel cup. Five mL of water was placed in the bottom of the bomb which was then assembled and pressurized to 30 atmospheres of oxygen. After combustion, the bomb was allowed to cool for 10 minutes and then slowly opened. The inside walls of the bomb were washed with water and all the washings were combined together, filtered if necessary, and diluted to 50 mL. The residue in the cup was dried at 110°C for 15 minutes and reweighed for ash determination.

Claissé Fluxer Fusion Device

The detailed procedure is described by Botto (9). This is an automated device which simultaneously fuses six samples. In this procedure, the finely powdered sample was mixed with ten

times its weight of lithium metaborate in a platinum crucible and heated at $\sim 950^{\circ}\text{C}$ for 15 minutes. The melt was dissolved in either dilute HCl or HNO_3 and the elements of interest were then determined by AAS or ICPES. Phosphorus was determined from the same solution by a separate molybdenum blue colorimetric procedure.

Inductively Coupled Plasma Emission Spectrometer

Details of our instrumentation are given by Botto (10). It is a Jarrell-Ash AtomComp Model 750 with 34 elemental channels. A list of these elemental channels, the wavelengths used for the determinations, the detection limits and the upper dynamic range for each element is given in the above paper. Six of the elemental channels are also focussed on weaker lines of lesser sensitivity for determining the higher elemental concentrations. This eliminates the necessity of diluting the samples further to prevent major elements in shale from exceeding the upper dynamic limit. The data from ICPES are processed by an on-line PDP-8M computer interfaced to a HP-1000 off-line computer.

Ion Chromatograph

A Dionex Model 14 was used for the determination of anions. The working parameters are given elsewhere (20). Quantitation was done by comparing the peak heights on the strip-chart recorder of the standards with the sample solutions.

Other Instrumentation

An Orion model 901 microprocessor ion analyzer was used for pH and for ion selective electrode measurements. A Norelco PW-1212 was used for X-ray fluorescence measurements. Certain of the ICPES results were checked with an Instrumentation Lab 951 atomic absorption spectrophotometer. Carbon, hydrogen and nitrogen were determined using a Hallikainen CH analyzer or Leco CHN-600 analyzer. Sulfur was determined using a Leco SC-32 analyzer. Oxygen was determined using 14 MeV neutron activation analysis.

Reagents

All of the acids used in this work were of "Ultrex" quality from J. T. Baker Chemical Company. Deionized water was obtained from a Millipore Corporation MilliQ system. An ICPES scan of this water showed a total of 33 elements to be ~ 1 ppm or less. Oil shale standards were provided by Dr. F. J. Flanagan of the U. S. Geological Survey. These were dried for 2 hours at 110°C before analysis.

RESULTS AND DISCUSSION

Ashing of Oil Shales

Because of potential difficulties due to carbonate content of the shales, the normal ASTM ashing procedure for coals was evaluated to find the optimum ashing temperature with minimum elemental losses for shales. A Green River oil shale was ashed at 750°C for 15 hours and then successively ashed for 3 hours each at 850, 950 and 1050°C . From each stage, the percentage ash was determined. All of these ashes and the original shale sample were analyzed for their carbonate content by evolution-gravimetry and for elemental composition by ICPES. The results are summarized in Table I. Essentially all of the carbonate is decomposed at 750°C ; heating further up to 1050°C showed no loss of any element determined. Thus, it seems feasible that a shale sample can be heated overnight to $\sim 800^{\circ}\text{C}$ and the ash subsequently analyzed for the elements of interest with good precision. Thermogravimetric analysis of a Colorado oil shale also indicated $\sim 850^{\circ}\text{C}$ as the optimum temperature for carbonate decomposition in shale.

The Parr oxygen bomb can be used if only a rapid ash determination is desired. The residue left in the ignition cup is equivalent to the ash content of a given shale. Having water as an absorbant in the bomb is not necessary; however, if water absorbant is used, it is probably better to dry the residual ash before final weighing to remove the moisture. Pressing the shale sample into a pellet helps in achieving uniform combustion and in reducing the risk of some sample being blown out of the cup during combustion. Typical results on two raw shales and two shale oil samples are given in Table II. The agreement between the values by the ASTM method for coals and the proposed method is very good (accuracy between 0.2 and 5% with an average of 4%). The precision of the method varies from 0.6 to 13% with an average relative standard deviation of 5%. Thus, the Parr oxygen bomb method can be used for a quick ash determination of coal or shale in a pilot plant laboratory situation as an alternative to the time-consuming ASTM D-3174 procedure.

Claissse Fluxer Analysis

Lithium tetraborate or metaborate fusion for the dissolution of rocks has been in use for many years. The Claissse Fluxer fusion device simply makes this fusion automated. We have used

the method in the past for the fusion of coal and fly ashes (9, 11). Oil shales can be dissolved by this method without pre-ashing. Once the solution is prepared, it may be analyzed for the most part by ICPEs or by AAS. Analysis of U.S.G.S. Devonian Ohio shale SDO-1 by Claisse fluxing followed by AAS or ICPEs measurements is illustrated in Table III.

TABLE I
ANALYSIS OF COLORADO OIL SHALE

Ashing Temperature, °C	Unashed	750	850	950	1050
Ash, wt %	-	63.1	62.8	62.6	61.9
CO ₃ , %	26.4	0.81*	0.42*	0.27*	0.19*
Al, %	3.30	3.15	3.15	3.18	3.14
Ba, wppm	502	515	516	512	513
Ca, %	12.0	12.5	12.8	12.3	12.7
Cr, ppm	31	33	29	24	35
Cu, ppm	134	133	130	136	126
Fe, %	1.69	1.64	1.63	1.62	1.61
K, %	0.98	1.00	0.97	0.95	0.95
Li, ppm	48	50	49	51	49
Mg, %	2.85	2.71	2.85	2.78	2.79
Mn, ppm	302	282	283	282	277
Na, %	1.37	1.35	1.35	1.34	1.36
P, %	0.12	0.11	0.11	0.10	0.10
Si, %	10.7	10.5	10.5	10.6	10.8
Sr, ppm	762	726	738	726	722
Ti, %	0.12	0.10	0.11	0.12	0.12
V, ppm	55	68	56	50	78
Zn, ppm	79	85	79	85	78

* Remaining in ash.

TABLE II
ASH DETERMINATION BY PARR OXYGEN BOMB

Wt % Ash by: Sample	High Temperature Ashing	Parr Oxygen Bomb*
Colorado Shale	62.8	62.7±0.4 (5)
Colorado Shale	72.7	72.2±0.4 (2)
Australian Shale Oil	1.80	1.72±0.11 (3)
Australian Shale Oil	1.87	1.64±0.21 (3)

* Number of replicate analysis.

In the predominantly AAS scheme, phosphorus and titanium are colorimetrically determined. The results obtained on five replicates of the solution by each method are given in Table III and are compared with the values obtained for this standard at the Indiana Geological Survey (7). The ICPEs and AAS results are in very good agreement with each other and with the literature values. The precision and the accuracy of the measurements are ±5% for most elements analyzed.

Combining the Claisse Fluxer fusion with ICPEs measurements gives a rapid and accurate method for the ash element analysis. The total analysis time is reduced to 20-25 minutes per sample. However, although the Claisse Fluxer procedure is excellent for the determination of all major elements, it is not suitable for the determination of trace elements, because the final solution (1 L) is too dilute for detection of trace elements. If the solution volume is kept small, extremely high concentrations of lithium and boron in the solution give an undesirable high background spectrum for trace element measurements. Hence, it is necessary to resort to a separate procedure where both trace and major elements can be simultaneously determined.

TABLE III

ANALYSIS OF SHALE SDO-1 BY CLAISSE FLUXER ICPES-AAS

Oxide Wt % by:	ICPES	AAS	Literature (7)
Al ₂ O ₃	15.6±0.15	15.2±0.12	15.6
CaO	1.37±0.02	1.33±0.01	1.42
Fe ₂ O ₃	11.8±0.1	11.7±0.1	12.2
K ₂ O	4.13±0.12	4.00±0.06	4.23
MgO	1.91±0.02	1.86±0.00	1.87
Na ₂ O	0.46±0.01	0.44±0.00	0.52
SiO ₂	62.4±0.6	63.7±1.1	64.4
TiO ₂	0.87±0.01	0.97	0.90
P ₂ O ₅	0.37±0.07	0.18	0.14
BaO	0.05±0.01	-	0.055
MnO	0.06±0.00	-	0.056
TOTAL	99.0	99.4	101.3

Parr Bomb Dissolution of Shales

Originally the so-called Parr bomb was developed by Bernas (12) for the dissolution of silicate matrices. The bomb is now marketed by Parr Instrument Company of Moline, Illinois. The dissolution procedure has been adapted to shales and consists of mixing 100 to 200 mg of the sample in 2 mL aqua regia and 2 mL HF. After the dissolution, 1 g of boric acid is added to each sample and the samples are heated in a waterbath for 15 minutes. If any unburned carbon is visible at this stage, the solutions are filtered; otherwise, the solutions are diluted to 100 mL for analysis by ICPES. A blank is used throughout the analysis scheme containing the same amounts of aqua regia, HF and boric acid and is used for intensity background corrections in the ICPES measurements.

Other workers have used different acid combinations for the dissolution of ashes in the Parr bomb. Thus, HCl + HF, HNO₃, HClO₄ + HF, aqua regia + HF, and HNO₃ + HClO₄ have all been used in the Parr bombs. We have found the aqua regia + HF mixture to be quite effective in accomplishing the dissolution. It is important to have a boric acid blank subtracted from the sample spectrum in the ICPES analysis to correct for the boron interferences with other elemental lines. It is also necessary to add boric acid to the sample solution immediately after opening the bomb and then to heat the solution on a waterbath for 15 minutes so that all of the boric acid goes in solution and reacts with insoluble fluorides. When boric acid was added only during the final dilution step, low recoveries were obtained, since Al, Ba, Ca and Mg, which form insoluble fluorides, were filtered off along with the unburned carbon.

The results of using the Parr bomb for shales are included in Table IV. These three shales are distributed by the U. S. Geological Survey as "standard" shales: Green River shale SGR-1, Cody shale SCO-1 and Devonian Ohio shale SDO-1. Not enough information is available in the literature on the composition of these shales. The U.S.G.S. values given in Table IV for shales SGR-1 and SCO-1 are averages of values from five papers given in an U.S.G.S. report (13), while the literature values for the shale SDO-1 are from the Indiana Geological Survey (7). We analyzed each sample in four replicates by the Parr bomb procedure. Overall, the agreement between the Parr bomb and the literature results is good. For SGR and SCO shales, chromium and nickel results could not be obtained by Parr bomb, due to contamination from the metal body of the bomb. Somewhat lower silicon results indicate partial volatilization of SiF₄ during dissolution. Phosphorus results for all three shales are lower than the literature values. If phosphorus is partly present as an organic complex in the shale, it will not be totally decomposed by the dissolution procedure.

The Parr bomb dissolution method seems to give satisfactory results on unashed oil shale samples. However, when the method was used for shales which had organic content greater than 20 wt %, lower recoveries for many elements were observed. Agreement between the data on the ashed samples by Claisse Fluxer and the unashed samples by the Parr bomb dissolution was poor, with the latter data always being low. The higher the kerogen content of the shales, the greater the discrepancy. We hypothesize that the mineral matter surrounded by kerogen results in poor

contact between the dissolving acids and the inorganic material, thus, resulting in the low recoveries. Ashing of these kerogen-enriched fractions eliminated this problem. The results in Table V for a typical Green River oil shale concentrate compare the data between the Claisse Fluxer and the Parr bomb methods, the latter with and without preashing. While agreement for the unashed sample is poor, the data from the ashed sample are in good agreement with the Claisse Fluxer procedure. The kerogen concentrates prepared by acid demineralization are analyzed for metals by ICPES after ashing the sample and dissolving it in aqua regia + HF. Typical analyses of an Australian oil shale and the kerogen isolated from it are given in Table VI. Drastic reduction in the metals content of the shale during the kerogen preparation is indicated. Almost complete demetallization of the major metals such as aluminum, calcium and silicon is evident. Pyrite, FeS_2 , is the only mineral left in the kerogen concentrate, since only HNO_3 will dissolve it. The elevated levels of fluorine and chlorine in the kerogen compared to the shale, originate from the HCl and HF used for the demineralization. Shale oils are "wet"-ashed with concentrated H_2SO_4 on a hot plate and in a muffle furnace before ICPES analysis for metals.

TABLE IV
ANALYSIS OF OIL SHALES BY PARR BOMB DISSOLUTION

Element, wppm	SGR-1		SCO-1		SDO-1	
	Parr Bomb	USGS ¹³	Parr Bomb	USGS ¹³	Parr Bomb	IGS ⁷
Al, %	3.31±0.27	3.71	7.39±0.17	7.23	6.43±0.25	6.4
As	25-40	75	<13	10.8	-	-
Ba	259±6	337	558±10	594	373±16	-
Be	0.5-1.0	0.91	0.4-2.3	1.58	<0.4	-
Ca, %	6.52±0.12	5.64	2.03±0.07	1.92	0.84±0.04	0.78
Cd	10.3±2.7	-	21.7±2.3	-	-	3
Co	13.5±4.5	11.6	<3	10.3	26±41	-
Cr	-	-	-	64.7	59±9	66
Cu	76±8	65.2	34±3	29.7	58±1	66
Fe, %	1.59±0.05	2.25	3.17±0.07	3.87	6.33±0.68	6.83
K, %	1.26±0.02	1.38	2.00±0.12	2.25	1.92±0.12	2.77
Mg, %	2.28±0.05	2.67	1.56±0.04	1.53	0.93±0.07	0.88
Mn	230±6	295	396±8	444	327±25	325
Mo	36-70	36	<10	2.79	146±5	156
Na, %	2.36±0.08	2.11	0.71±0.04	0.66	0.23±0.03	0.30
Ni	-	34.3	-	29.1	119±18	105
P	562±22	1540	429±33	860-1900	138±36	436
Si, %	11.8±0.3	13.8	25.4±0.8	29.2	19.6±1.1	23.3
Ti, %	0.14±0.002	0.25; 0.069	0.36±0.01	0.37	0.44±0.03	0.42
V	114±3	124	119±4	116	156±7	157
Zn	85±3	79	99±5	108	76±9	71

TABLE V
EFFECT OF ASHING ON ELEMENT DETERMINATION IN GREEN RIVER SHALE CONCENTRATE

Element, wt %	Claisse Fluxer	Parr Bomb	
		No Ashing	Preashing
Si	11.6	7.04	11.2
Al	3.09	2.28	2.97
Fe	1.76	1.30	1.71
Mg	1.36	1.02	1.18
Ca	4.78	3.75	4.37
Na	1.39	1.05	1.32
K	0.92	0.56	0.88
Ti	0.13	0.03	0.092
P	0.24	0.10	0.15

Determination of Nonmetals

Ion chromatography (IC) has been used for the determination of fluorine, chlorine, nitrogen and sulfur in oil shales and shale oils. This determination also requires dissolution using the

Parr bomb technique to bring the sample into aqueous solution. Determination of these elements in coal analyses has been described previously (3) where the halogens were determined with ion selective electrodes, nitrogen with a chemiluminescent detector and sulfur by X-ray fluorescence. However, all these elements can be simultaneously determined by IC. With the fast separator columns and 0.0024 M Na_2CO_3 + 0.0030 M NaHCO_3 eluent at 2.30 mL/min flow rate, the retention times for F^- , Cl^- , NO_3^- and SO_4^{2-} were found to be 2.5, 3.5, 9 and 10.5 minutes, respectively. Thus, in less than 15 minutes, four anions can be quantitatively determined; significantly less time than required by the other specific techniques. Typical IC results for the shales are given in Table VII. The difficulty of accurately determining the halogens in the rock matrix is evident from the disagreement between the various literature results for the U.S.G.S. standard shales. Previously using this method on coal samples, good agreement was obtained between certified and IC results (20). Unfortunately, the shale standards have not been extensively analyzed and reported in the literature to enable one to form a true picture of their halogen concentrations. The sulfur results by Parr bomb-IC are in good agreement with the published data.

TABLE VI
ANALYSIS OF AUSTRALIAN SHALE AND KEROGEN

Element, ppm	Shale	Kerogen
Al	6.28%	225
As	-	16
Ba	315	14
Ca	1.13%	391
Cl	412	7070
Co	8.6	9
Cr	34	8.9
Cu	34	81
F	604	1800
Fe, %	4.26	2.66
K	9580	25
Li	28	22
Mg	7040	50
Mn	875	19
Na	4860	132
Ni	41	31
Si	17.0%	107
Ti	1880	12
V	98	-
Zn	97	61

TABLE VII
ION CHROMATOGRAPHIC ANALYSIS HALOGENS AND SULFUR IN OIL SHALES

Sample	Fluorine, ppm		Chlorine, ppm		Sulfur, %	
	Literature	Found ^a	Literature	Found ^a	Literature	Found ^a
U.S.G.S. SGR-1	2285 (14)	307±36	92 (14); 45 (15)	1400±87	1.90 (15); 1.64 (14)	1.71±0.05
U.S.G.S. SCO-1	1500 (16); 779 (14, 17)	425±37	1600 (16); 68 (15); 49 (14)	742±26	0.12 (16) 0.06 (14, 15)	0.052±0.001
Green River Kerogen, %	0.22 ^b	0.25	1.64 ^b	1.48	2.68 ^b	2.42

a. Shale results mean of triplicate analysis.

b. Fluorine and chlorine were determined by ion selective electrodes after Parr bomb combustion, and sulfur was determined by Leco SC-32.

Determination of Carbon, Hydrogen and Nitrogen

Methods for the determination of these elements are based on the combustion of oil shale

samples, usually at 1000°C and measuring the CO₂, H₂O and N₂ produced, by different techniques after scrubbing from the gases the halogens, SO₂ and excess oxygen. Various instruments use gravimetry, infrared, or thermal conductivity for final measurements. Comparative performance of several C/H instruments is illustrated in Table VIII. All appear to give reasonably satisfactory results for carbon and hydrogen. The precision of the results appears to be of the order of $\pm 1\%$ of the C, H, N values.

TABLE VIII
DETERMINATION OF CARBON/HYDROGEN IN OIL SHALES

<u>Instrument</u>	<u>Colorado Shale</u>	<u>Australian Shale</u>
<u>Carbon, Wt %</u>		
Hallikainen	20.4 \pm 0.06 (3)	14.4 \pm 0.10 (3)
Leco CHN-600	20.1 \pm 0.11 (28)	14.04 \pm 0.06 (28)
Leco CR-12	19.8 \pm 0.5 (3)	13.6 \pm 0.17 (3)
Perkin Elmer	20.0 \pm 0.10 (3)	13.7 \pm 0.17 (3)
ASTM Combustion	20.4 \pm 0.12 (3)	14.2 \pm 0.17 (3)
<u>Hydrogen, Wt %</u>		
Hallikainen	2.24 \pm 0.01 (3)	2.24 \pm 0.01 (3)
Leco CHN-600	2.15 \pm 0.04 (28)	2.18 \pm 0.04 (28)
Perkin Elmer	2.10 \pm 0.03 (3)	2.16 \pm 0.02 (3)
ASTM Combustion	2.25 \pm 0.02 (3)	2.31 \pm 0.02 (3)

Numbers in parentheses are the replicate number of analyses.

The classical method for nitrogen determination is the Kjeldahl procedure. The method is very precise and well characterized. However, recently, we have found this method to give erroneously low nitrogen results for some oil shale samples. The data in Table IX illustrate this problem. Two samples of Colorado and Australian shales were analyzed by the Kjeldahl procedure in five different laboratories. The same samples were also analyzed by four different instruments in three different laboratories. Good agreement is apparent among all methods for the Australian shale, but for the Colorado shale there are significant differences. The results can be subgrouped as (a) Kjeldahl data and (b) instrumental data. All of the Kjeldahl results are close, but they are low roughly by a factor of 2 compared to the instrumental techniques. The different instruments have also produced remarkably close results. We believe the non-aminoid nitrogen compounds present in the oil shales are not being determined by the Kjeldahl procedure. Attempts to obtain higher Kjeldahl results by more vigorous digestion did not succeed. We believe it is advisable to use the instrumental methods rather than the Kjeldahl procedure for the determination of true nitrogen content of oil shales. The fact that the Australian shale gave equivalent results by chemical and instrumental methods, but the Colorado shale did not, probably indicates the presence of different specific nitrogen compounds in oil shales as a result of their different genesis.

Determination of Sulfur Forms

A knowledge of the forms and the concentrations of sulfur present in the oil shales is desirable for determining the composition, heating value, thermal degradation properties and eventually relating the sulfur forms found in the shale to those found in the oil. The separation and analysis methods were primarily developed for coal products (ASTM D-2492 procedure). However, when applied to oil shales, this procedure has resulted in reproducible but erroneous results. Smith, et al (18) have pointed out the drawbacks of this procedure and have devised a new procedure based on the HC10₄ dissolution of sulfate and LiAlH₄ reductive dissolution of pyrite. However, many of the laboratories in the U. S. are still using the ASTM procedure. We found the ASTM method to overestimate the sulfate and pyrite forms, thus, resulting in underestimating organic sulfur, even giving negative values in some cases. Our attempts to obtain better results by using a variety of other decomposition aids have not met with success so far. We have been reluctant to apply the U. S. B. M. procedure (18) in our laboratory on a routine basis because of the hazardous nature of HC10₄ and particularly LiAlH₄. The best alternative to the ASTM and U. S. B. M. procedures appears to be the demineralization-kerogen isolation procedure for the determination of pyrite. This U. S. B. M. procedure (19) uses HCl-HF to remove the carbonate and the silicate minerals in the shales, leaving the kerogen residue with only pyrite as the mineral contaminant. In the proposed pyrite determination procedure, this isolated kerogen is analyzed for its iron content by

dissolution in HNO_3 and subsequent AAS or ICPES measurement. A single analysis carried out by this procedure on two shale samples gave results that were definitely lower than the ASTM procedure, but much closer to the LiAlH_4 procedure (Table X). Further work needs to be carried out to determine the quantitative validity of the isolated kerogen procedure.

TABLE IX
DETERMINATION OF NITROGEN IN OIL SHALES

Method	Wt % N	
	Colorado Shale	Australian Shale
Kjeldahl-Lab A	0.42+0.02 (3)	0.38+0.01 (3)
Kjeldahl-Lab B	0.40+0.01 (3)	0.38+0.01 (3)
Kjeldahl-Lab C	0.42+0.00 (3)	0.39+0.02 (3)
Kjeldahl-Lab D	0.49+0.01 (3)	0.41+0.01 (3)
Kjeldahl-Lab E	0.50+0.05 (2)	0.57+0.01 (2)
Leco NP-28	0.70+0.01 (3)	0.42+0.01 (3)
Leco CHN-600	0.79+0.004 (28)	0.57+0.04 (28)
Perkin Elmer	0.79+0.05 (3)	0.46+0.03 (3)
Mettler	0.65+0.02 (3)	0.43+0.01 (3)
Mean-All	-	0.46+0.08
Mean-Kjeldahl (a)	0.45+0.05	0.43+0.08
Mean-Instrumental (b)	0.74+0.06	0.47+0.07
ASTM Kjeldahl Repeatability	0.05	0.05

Numbers in the parentheses are the replicate number of analyses.

TABLE X
DETERMINATION OF PYRITE IN OIL SHALES

Method (Replicates)	Colorado Shale	Australian Shale
ASTM (11)	0.68+0.09	0.79+0.07
LiAlH_4 (3)	0.43+0.02	0.64+0.01
Demineralization (1)	0.41	0.48

In summary, the methods developed using ICPES and IC and other thermal decomposition procedures for metals and nonmetals, are now routinely used at Exxon's Baytown Research and Development Division for the characterization of a large number of oil shales and shale products.

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LITERATURE CITED

- (1) Culbertson, W. C. and Pitman, J. K., U.S.G.S. Prof. Paper, 820, 497-503 (1973).
- (2) Nadkarni, R. A., Anal. Chem., 52, 929-935 (1980).
- (3) idem, Amer. Lab., 13 (8), 22-29 (1981).
- (4) idem, Anal. Chim. Acta., 135, 363-368 (1982).
- (5) Fruchter, J. S., Wilkerson, C. L., Evans, J. C. and Sanders, R. W., Environ. Sci. Technol., 14, 1374-1381 (1980).
- (6) Shendrikar, A. D. and Faudel, G. B., ibid., 12, 332-334 (1978).
- (7) Lechler, P. J. and Leininger, R. K., Jarrell-Ash Plasma Newslett., 2 (1), 8-10 (1979).
- (8) Amini, M.K., DeFreese, I. D. and Hathaway, L. R., Appl. Spectrosc., 35, 497-501 (1981).
- (9) Botto, R. I., Jarrell-Ash Plasma Newslett., 2 (2), 4-8 (1979).
- (10) idem, Proc. Int. Conf. Dev. At. Plasma Spectrochem. Anal., Puerto Rico, in press (1980).
- (11) Nadkarni, R. A., Botto, R. I. and Smith, S. E., At. Spectroscopy (in press).
- (12) Bernas, B., Anal. Chem., 40, 1682-1686 (1968).
- (13) Flanagan, F. J., U.S.G.S. Prof. Paper, 840 (1976).
- (14) Evans, K. L., Tarter, J. G. and Moore, C. B., Anal. Chem., 53, 925-928 (1981).
- (15) Fabbi, B. P. and Espos, L. F., U.S.G.S. Prof. Paper, 840, 89-93 (1976).
- (16) Schultz, L. G., Pourtelot, H. A. and Flanagan, F. J., U.S.G.S. Prof. Paper, 840, 21-23 (1976).
- (17) Malchacek, V., Rubeska, I., Sixta, V. and Sulcek, Z., U.S.G.S. Prof. Paper, 840, 73-77 (1976).
- (18) Smith, J. W., Young, N. B. and Lawlor, D. L., Anal. Chem., 36, 618 (1964).
- (19) Smith, J. W., U. S. Bureau of Mines Rept. Investig. (1961).
- (20) Nadkarni, R. A., Anal. Chim. Acta (accepted for publication).